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Thermodynamics of hard-core molecular fluids with Yukawa-tail

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Abstract : The thermodynamic properties of hard-core molecular fluid with a Yukawa tail are determined theoretically.The calculated properties, such as the equation of state and internal energy are compared with the molecular dynamics and Monte Carlo results where they are available. The agreement is found to be good

Keywords : Yukawa tail fluid, thermodynamic properties, simulation results

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1. Introduction

In recent years, hard-core fluid withYukawa tail has been a subject of growing interest [1-6]. This is because the fluid with Yukawa tail has proved to be a very useful solvable model, which represents qualitatively the thermodynamic and structural properties of a real fluid [1,6]. However, this interest is confined to the simple Yukawa fluid (*i.e.* the simple hard core fluid with Yukawa tail). No attempt has been made to study a molecular fluid with a potential model having an attractive Yukawa tail.

In this paper, we study the thermodynamic properties of molecular fluid of molecules interacting *via* the hard-core plus Yukawa tail potential. The Yukawa tail potential with

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parameter $z = 1.8/\sigma$ is a reasonable model for real simple fluid [1]. Moreover, the complicating effects due to a softness of the repulsive part of potential are not present in this model.

For classical molecular fluids, one of the most successful approaches is the perturbation theory [7]. For hard-core molecular fluids, the perturbation expansion is made about the hard Gaussian overlap (HGO) reference system [8]. Recently, Boublik [9] and Singh *et al* [10] have generalised the Barker Henderson (BH) perturbation theory [11] to calculate the equilibrium properties of the non-spherical molecular fluids. In the present work, we employ the generalized BH theory in the local compressibility (1c) approximation for evaluating thermodynamic properties of the molecular Yukawa fluid and compare with the simulation results where they are available.

In Section 2, we describe the perturbation theory for evaluating the thermodynamic properties of hard-core molecular fluid in which the intermolecular potential consists of a hard Gaussian overlap and an attractive Yukawa tail. The results are discussed in Section 3.

2. Perturbation expansion

In this section, we consider the classical molecular fluid, whose molecules interact *via* the hard-core plus Yukawa tail potential defined as

$$u(r, \omega_1, \omega_2) = \infty, r < \sigma(\omega_1, \omega_2)$$

$$= -\varepsilon(\omega_1, \omega_2) \frac{\exp[-z\{r - \sigma(\omega_1, \omega_2)\}]}{r/\sigma(\omega_1, \omega_2)}, \quad r > \sigma(\omega_1, \omega_2) \tag{1}$$

where $\sigma(\omega_1,\omega_2)$ is the distance of closest approach between two molecules. Here $r = |r_1 - r_2|$ and ω_2, is the orientation of molecule i. In eq. (1), $\sigma(\omega_1, \omega_2)$ and $\varepsilon(\omega_1, \omega_2)$ are angle-dependent range and strength parameters, respectively. They are given by [12]

$$\sigma(\omega_1, \omega_2) = \sigma_0 \left[1 - x \frac{\cos^2\theta_1 + \cos^2\theta_2 - 2x\cos\theta_1\cos\theta_2\cos\theta_{12}}{1 - x^2\cos^2\theta_{12}}\right], \tag{2}$$

$$\varepsilon(\omega_1\omega_2) = \varepsilon_0[1 - x^2\cos^2\theta_{12}]^{-1/2}, \tag{3}$$

ε_0 and σ_0 are constants with units of energy and length respectively, and the shape parameter x is defined as

$$x = \left(x_0^2 - 1\right)/\left(x_0^2 + 1\right), \tag{4}$$

x^0 being the length-to-breadth ratio of the molecule.

We divide the pair potential $u(r,\omega_1,\omega_2)$ as

$$u(r, \omega_1\omega_2) = u_{HGO}(r, \omega_1\omega_2) + u_p(r, \omega_1\omega_2), \tag{5}$$

where

$$u_{HGO} \quad (r, \omega_1 \omega_2) = \infty, \; r < \sigma(\omega_1, \omega_2)$$

$$= 0, \; r > \sigma(\omega_1, \omega_2) \tag{6}$$

is the hard Gaussian overlap (HGO) potential treated as a reference potential and

$$u_p(r, \omega_1, \omega_2) = -\varepsilon(\omega_1, \omega_2) \frac{\exp[-z\{r - 6(\omega_1, \omega_2)\}]}{r / \sigma(\omega_1, \omega_2)} \tag{7}$$

is a perturbation. The dependence of ε on the orientation is weak and in the special case (GOCE) [13],

$$\varepsilon(\omega_1, \omega_2) \approx \varepsilon_0.$$

Using this division of the pair potential, the perturbation expansion of the residual Helmholtz free energy can be written as

$$\frac{A - A^*}{NkT} = \frac{A_{HGO} - A^*}{NkT} + (\beta\varepsilon_0)\frac{A_1}{NkT} + (\beta\varepsilon_0)^2 \frac{A_2}{NkT} + \ldots\ldots, \tag{8}$$

where A^* is the Helmholtz free energy of an ideal gas and $A_{HGO}-A^*$ is the residual free energy of the HGO fluid (*i.e.* the reference fluid). A_1 and A_2 are the first and second order perturbation correction terms. The residual free energy of the HGO fluid is given by [14]

$$\frac{A_{HGO} - A^*}{NkT} = \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} F_1(x), \tag{9}$$

where $$F_1(x) = (1 - x^2)^{-1/2}[1 - (1/6)x^2 - (1/40)x^4 - (1/112)x^6\ldots\ldots] \tag{10}$$

and the packing fraction.

$$\eta = \rho v_{HC} = \frac{\pi}{6} (\rho\sigma_0^3) x_0, \tag{11}$$

V_{HC} being the volume of a HGO molecule. The first and second order perturbation correction terms are given by

$$\frac{A_1}{NkT} = \frac{1}{2}\rho \int dr < g_{HGO}(r, \omega_1, \omega_2) \; u_p(r, \omega_1, \omega_2)/\varepsilon_0 > \omega_1, \omega_2 \tag{12}$$

$$\frac{A_2}{NkT} = -\frac{1}{4}\frac{\rho}{\beta}\left(\frac{\partial\rho}{\partial\rho_{HGO}}\right)\frac{\partial}{\partial\rho}\left[\rho \int dr < g_{HGO}(r, w_1, w_2) \right.$$

$$\left.\left\{u_p(r, \omega_1, \omega_2)/\varepsilon_0\right\}^2 > \omega_1, \omega_2\right] \tag{13}$$

where $g_{HGO}(r, \omega_1, \omega_2)$ is the pair correlation function (PCF) of the HGO fluid.

Using eq.(5), the PCF of the classical molecular fluid can be written as

$$g(r,\omega_1,\omega_2) = g_{HGO}(r,\omega_1,\omega_2) + \beta\varepsilon_0 g_1(r,\omega_1,\omega_2) + \ldots\ldots, \tag{14}$$

where $g_1(r,\omega_1,\omega_2)$ is the first order perturbation correction to the PCF. Eq. (14) can be used to obtain the perturbation expansion (8) for the Helmholtz free energy. Where

$$\frac{A_2}{NkT} = -\frac{1}{4}\rho \int d\bar{r} < g_1(r,\omega_1,\omega_2)\, u_p(r,\omega_1,\omega_2)/\varepsilon_0 > \omega_1 a \tag{15}$$

comparing eqs. (13) and (15), we get

$$< g_1(r,\omega_1,\omega_2)\, u_p(r,\omega_1,\omega_2)/\varepsilon_0 > \omega_1\omega_2$$

$$= -\frac{1}{\beta}\left(\frac{\partial\rho}{\partial\rho_{HGO}}\right)\frac{\partial}{\partial\rho}\Big[\rho < g_{HGO}(r,\omega_1,\omega_2)$$

$$\left\{u_p(r\,\omega_1\,\omega_2)/\varepsilon_0\right\}^2 > \omega_1,\omega_2\Big]. \tag{16}$$

Eq. (16) is not expected to provide good results for the PCF [11]. However, it may be used to calculate the PCF at the core.

In order to evaluate the perturbation correction terms, we use the decoupling approximation [15] and introduce the new variable $r^* = r/\sigma(\omega_1,\omega_2)$. Then the potential (1) is transfers to the central form *i.e.* the hard sphere plus Yukawa tail potential. Consequently, in the simplest approach, the molecular pair correlation function of HGO fluid is [14,15]

$$g_{HGO}(r,\omega_1,\omega_2) \approx g_{HGO}\left(r/\sigma(\omega_1,\omega_2)\right) \approx g_{HS}(r^*), \tag{17}$$

where $g_{HS}(r^*)$ is the PCF of the hard-sphere (HS) fluid at the packing fraction $\eta = \rho v_{hc}$. Then eqs. (12) and (13) can be expressed in simpler forms

$$\frac{A_1}{NkT} = 12\eta F_1(x)\int g_{HS}(r^*)u_p^*(r^*)r^{*2}dr^*, \tag{18}$$

$$\frac{A_2}{NkT} = -\frac{6}{a_{HGO}}\eta F_1(x)\frac{\partial}{\partial\eta}\left[\eta\int_1 g_{HS}(r^*)u_p^{*2}(r^*)r^{*2}dr^*\right], \tag{19}$$

where [10]

$$a_{HGO} = \beta\left(\frac{\partial P_{HGO}}{\partial\rho}\right) = 1 + \frac{2\eta(4-\eta)}{(1-\eta)^4}F_1(x), \tag{20}$$

$u_p^* = u_p/\varepsilon_0$. For $x_0 = 1$. $F_1(x) = 1$ and a_{HGO} becomes a_{HS}.

The integrals appearing in eqs. (18) and (19) can be evaluated numerically.

3. Results and discussions

We calculate the thermodynamic properties such as the equation of state, residual free energy and configurational internal energy of the molecular Yukawa fluid with $z = 1.8/\sigma$ for different values of anisotropy parameters x_0 (*i.e.* $0 < x_0 < 2.0$). We choose this value of z, since the Yukawa fluid with $z = 1.8/\sigma$ is a qualitatively reasonable model for real fluids [1,6] and the simulation results are available in some cases for such a fluid.

The values of A_1/NkT and A_2/NkT are reported in Figure 1 as function of the parameter x_0 at ρ^* ($= \rho\sigma_0^3$) = 0.3 and 0.5, which shows that the magnitude of the perturbation corrections increases with x_0 as well as with ρ^*. However, when the correction terms are considered as a function x_0 of at a given packing fraction (not shown in the figure), they are maximum at $x_0 = 1.0$ and decrease steadily as x_0 moves from 1.0. For a given η, each of A_1/NkT and A_2/NkT has the same value, for example, at $x_0 = 2.0$ and $x_0 = 1/2$.

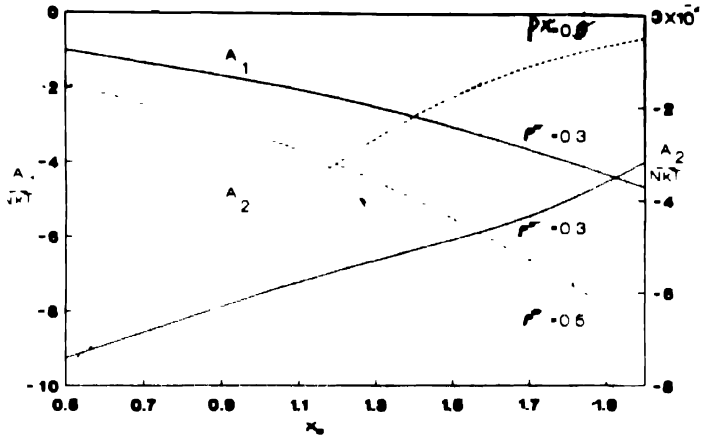

Figure 1. Values of A_1/NkT and A_2/NkT for the molecular Yukawa fluid ($z = 1.8/\sigma$) as a function of x_0 at $\rho^* = 0.3$ and 0.5.

The simulation results for the equation of state $P/\rho kT$ and configurational internal energy $U_l/N\varepsilon_0$ are available for the classical Yukawa fluid at $x_0 = 1.0$. We first present our results for this case and compare these with the molecular dynamic (MD) [6] and Monte Carlo (MC) [1] values for several densities and temperatures. In Table 1, we compare our results

Table 1. Equation of state, $P/\rho kT$ for the classical Yukawa fluid ($z = 1.8/\sigma$) at $x_0 = 1$.

ρ^*	T^*	Present Theory	MD	MC
0.3	2.0	0.975	0.97	–
	1.5	0.648	0.66	–
	1.0	–0.002	0.02	–
0.4	2.0	1.123	1.12	1.08
	1.5	0.664	0.67	0.69
	1.0	–0.246	–0.20	–0.21

Table 1. *(Cont'd)*

ρ^*	T^*	Present Theory	MD	MC
0.5	2.0	1.429	1.43	–
	1.5	0.825	0.81	–
	1.0	–0.372	–0.28	–
0.6	2.0	1.985	2.00	2.04
	1.5	1.226	1.22	1.21
	1.0	–0.281	–0.24	–0.27
0.7	2.0	2.925	2.07	–
	1.5	2.003	1.99	–
	1.0	0.170	0.19	–
0.8	2.0	4.459	4.46	4.27
	1.5	3.368	3.37	3.31
	1.0	1.195	1.17	1.29

for the equation of state, $P/\rho kT$ of the Yukawa fluid with $x_0 = 1.0$ with MD and MC values. The agreement is very good. This method is expected to provide good results even for other value of x_0. The value of $P/\rho kT$ as a function of ρ^* at $x_0 = 0.5$, 1.0 and 2.0 are shown in Figure 2, which shows the variation of the equation of state with x_0.

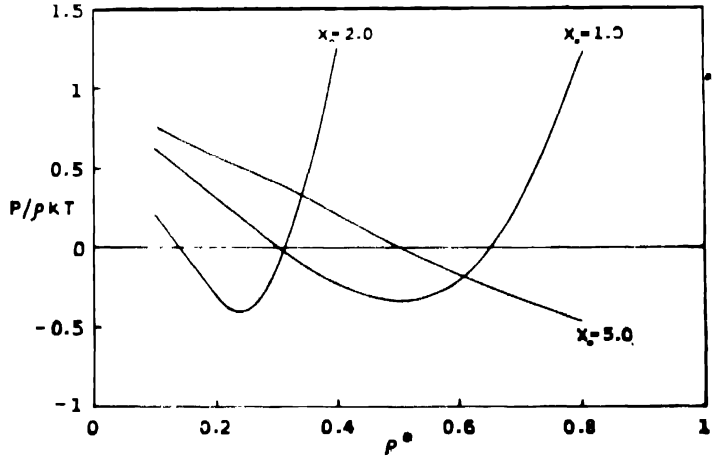

Figure 2. Equation of state $P/\rho kT$ for the molecular Yukawa fluid ($z = 1.8/\sigma$) as a function of ρ^* at $x_0 = 0.5$, 1.0 and 2.0 for $T^* = 1.0$.

Our results of the internal energy $U_t/N\varepsilon_0$ for the classical Yukawa fluid at $x_0 = 1.0$ are compared with the MD and MC values in Table 2 for different densities ρ^* and temperature $T^* = (\beta\varepsilon_0)^{-1}$. The agreement is found to be good. Here U_t is the excess internal energy with respect to the ideal gas at the same temperature and density. In Figure 3, we report the values of $U_t/N\varepsilon_0$ as a function of x_0 for $\rho^* = 0.4$ at $T^* = 1.0$ and 2.0. We find that the magnitude of the internal energy increases with increase of x_0.

Table 2. Configuration internal energy for the classical Yukawa fluid ($z = 1.8/\sigma$) at $x_0 = 1.0$.

ρ^*	T^*	Present Theory	MD	MC
0.3	2.0	−1.867	1.917	–
	1.5	−1.886	−1.956	–
	1.0	−1.925	2.114	–
0.4	2.0	−2.551	−2.586	2.583
	1.5	−2.570	−2.619	−2.622
	1.0	−2.608	−2.745	2.832
0.5	2.0	−3.260	−3.276	–
	1.5	−3.274	3.311	
	1.0	−3.303	−3.384	
0.6	2.0	−4.004	−4.033	−4.030
	1.5	−4.017	−4.045	−4.051
	1.0	−4.035	−4.079	−4.073
0.7	2.0	−4.780	−4.814	–
	1.5	−4.787	−4.820	–
	1.0	−4.802	−4.838	–
0.8	2.0	−5.586	−5.628	−5.622
	1.5	−5.590	−5.632	−5.630
	1.0	−5.599	−5.638	5.635

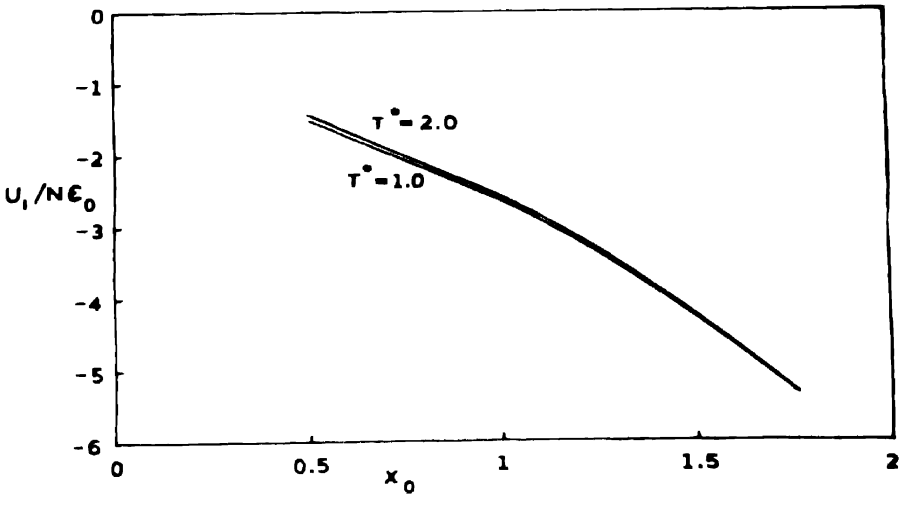

Figure 3. Internal energy $U_1/N\varepsilon_0$ for molecular Yukawa fluid ($z = 1.8/\sigma$) as a function of x_0 at $\rho^* = 0.4$ for $T^* = 1.0$ and 2.0

The contact values of the PCF $g(\sigma^+)$ for the Yukawa fluid with $x_0 = 1.0$ are reported in Table 3. The MD and MC results are also shown there. The agreement is good. This shows the validity of (16) for estimating $g(\sigma^+)$ for all values of x_0 considered.

Table 3. Value of $g(\sigma^+)$ for the class Yukawa fluid ($z = 1.8/\sigma$) at $x_0 = 1.0$.

ρ^*	T^*	Present Theory	MD	MC
0.3	2.0	1.870	1.967	–
	1.5	1.980	2.175	–
	1.0	2.201	2.780	–
0.4	2.0	2.107	2.172	2.128
	1.5	2.205	2.327	2.378
	1.0	2.402	2.811	2.943
0.5	2.0	2.425	2.446	–
	1.5	2.513	2.555	–
	1.0	2.689	2.952	–
0.6	2.0	2.851	2.901	2.921
	1.5	2.931	2.961	2.966
	1.0	3.090	3.228	3.205
0.7	2.0	3.429	3.495	
	1.5	3.501	3.533	
	1.0	3.645	3.685	–
0.8	2.0	4.225	4.210	4.109
	1.5	4.291	4.261	4.257
	1.0	4.423	4.382	4.490

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